PB87-115713

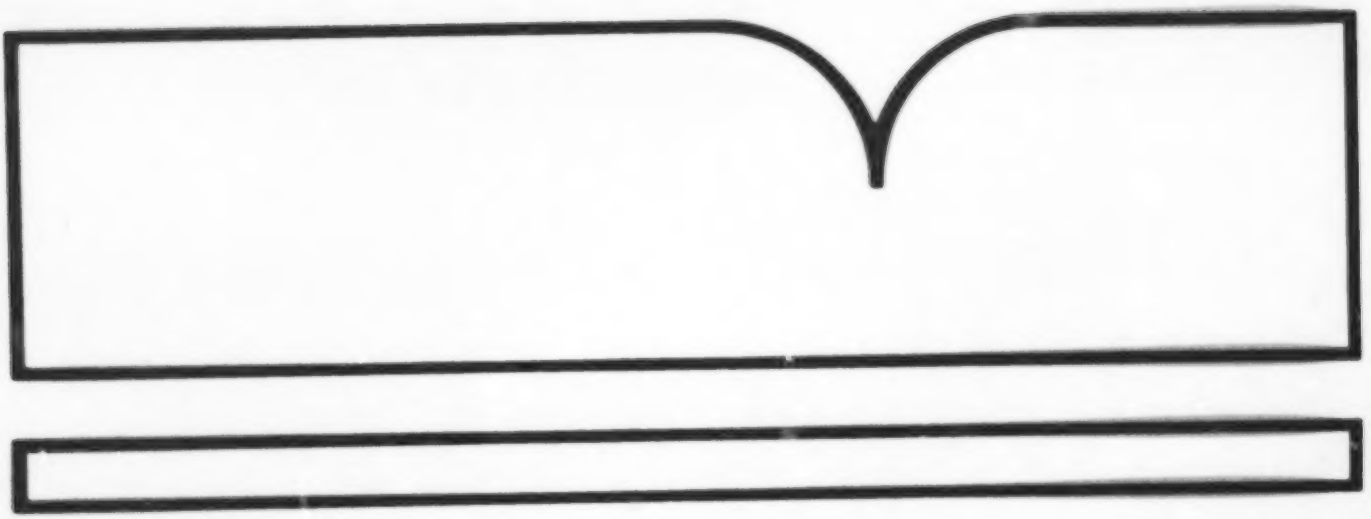
Influence of pH on the Removal of Organics by Granular Activated Carbon

Minnesota Univ., Minneapolis

Prepared for

Environmental Protection Agency
Cincinnati, OH

1986



U.S. Department of Commerce
National Technical Information Service
NTIS

PB87-115713

TECHNICAL REPORT DATA
(Please read Instructions on the reverse before completing)

1. REPORT NO. EPA/600/J-86/149	2.
3. RECIPIENT'S ACCESSION NO.	
4. TITLE AND SUBTITLE INFLUENCE OF pH ON THE REMOVAL OF ORGANICS BY GRANULAR ACTIVATED CARBON (Journal Version)	5. REPORT DATE 1986
	6. PERFORMING ORGANIZATION CODE
7. AUTHOR(S) M.J. Semmens, G.E. Norgaard, G. Hohenstein, and A.B. Staples	8. PERFORMING ORGANIZATION REPORT NO.
9. PERFORMING ORGANIZATION NAME AND ADDRESS University of Minnesota Minneapolis, MN 55455-0220	10. PROGRAM ELEMENT NO.
	11. CONTRACT/GRANT NO. CR806377
12. SPONSORING AGENCY NAME AND ADDRESS Water Engineering Research Laboratory- Cincinnati, OH Office of Research and Development U.S. Environmental Protection Agency Cincinnati, OH 45268	13. TYPE OF REPORT AND PERIOD COVERED Journal Article
	14. SPONSORING AGENCY CODE EPA/600/14

15. SUPPLEMENTARY NOTES
Project Officer, Leown Moore
Journal American Water Works Association, 78(5):89-93, May 1986

16. ABSTRACT
Studies with miniature columns of granular activated carbon (GAC) demonstrated the importance of pH in the removal of total organic carbon and trihalomethane precursors from coagulated Mississippi River water.

17. KEY WORDS AND DOCUMENT ANALYSIS

a. DESCRIPTORS	b. IDENTIFIERS/OPEN ENDED TERMS	c. COSATI Field/Group

18. DISTRIBUTION STATEMENT RELEASE TO PUBLIC	19. SECURITY CLASS *(This Report)* UNCLASSIFIED	21. NO. OF PAGES 7
	20. SECURITY CLASS *(This page)* UNCLASSIFIED	22. PRICE

EPA Form 2220-1 (Rev. 4-77) PREVIOUS I

REPRODUCED BY
U.S. DEPARTMENT OF COMMERCE
NATIONAL TECHNICAL
INFORMATION SERVICE
SPRINGFIELD, VA. 22161

EPA/600/J-86/149
JOURNAL ARTICLE

Influence of pH on the Removal of Organics by Granular Activated Carbon

Michael J. Semmens, Gregor E. Norgaard, Gary Hohenstein, and Alan B. Staples

Studies with miniature columns of granular activated carbon (GAC) demonstrated the importance of pH in the removal of total organic carbon and trihalomethane precursors from coagulated Mississippi River water.

Data from coagulation studies on Mississippi River water samples indicated that pH was a most important parameter in determining the extent of organics removal for a specified coagulant dose.[1] Performance curves indicated that optimum organics removal was attained with alum at a pH of between 5 and 6 and that as solution pH was raised into the neutral range, organics removal deteriorated dramatically. Similar observations are reported elsewhere.[2]

The adjustment of pH to more acidic values influences the speciation of aluminum and increases protonation of the organic acids that contribute to coagulant demand.[1,2]

The extent of organics removal that may be achieved by coagulation, however, is limited, and granular activated carbon (GAC) treatment may be required if low concentrations of organics are desired in the treated water. In such cases, conditions employed during pretreatment may have a profound influence on the subsequent performance and useful life of the GAC.

Experimental materials and methods

Water source. The water employed in this study was taken from the Mississippi River close to where water is extracted by the Minneapolis treatment plant. The Mississippi River arises from a peaty-swampy area and as a result is highly colored and rich in natural organics. The concentration of synthetic compounds at this point is minimal.

Pretreatment. Samples (26.4 gal [100 L]) of river water were transferred to a 36.9-gal (140-L) stainless-steel tank. The contents of the tank were mixed rapidly using a 180-W direct drive motor and stainless-steel impeller. The power input was controlled by coupling the stirrer to a variable autotransformer. The rapid mixer was mounted off-center and operated at sufficient speed to create a vortex. The appropriate coagulant dose was added by pouring a known volume of stock solution [50 g of either $Al_2(SO_4)_3 \cdot 18H_2O$/L or $Fe_2(SO_4)_3 \cdot 7H_2O$/L] into the vortex. Following 10 s of additional rapid mixing, the mixer was replaced with a flocculator. The flocculator consisted of a 90-W high-speed (500 rpm maximum) drive motor coupled to stainless-steel paddles through a 20:1 reduction gear. The speed of rotation was controlled with the variable transformer. The stirrer was equipped with three 11.8-in. × 1.3-in. (30-cm × 3.5-cm) stainless-steel paddles. The top of the stainless-steel shaft was tapped into a 0.5-in. (1.5-cm) clear acrylic rod to insulate the flocculator's contents. This was designed to prevent electrical interference created by the motor from affecting the measurement of solution pH.

Immediately after rapid mixing, pH was adjusted and the tank's contents were flocculated 30 min at 10–30 rpm.

Following flocculation, the contents of the tank settled for 1 h. The settled water was then pumped at 250 mL/min through a trimedia filter. The filter, which was contained in a 3.9-in. (10-cm) glass column, consisted of 9 in. (23 cm) of anthracite, 9 in. (23 cm) of sand, and 9 in. (23 cm) of garnet. The media were supported by 3.9 in. (10 cm) of graded gravel on a coarsely sintered glass disc. The first 0.7 gal (3 L) of filtered water was discarded, and the remainder was collected in covered 10.5-gal (40-L) stainless-steel tanks. After filtration of each batch, the filter was backwashed with tap water for 10 min at 50-percent expansion.

Operation of the carbon column. The filtered water was pumped* to small columns,† which measured 0.3 in. × 11.8 in. (0.9 cm × 30 cm) and contained 2.3 to 3.5 in. (6 to 9 cm) of carbon‡ supported on 0.7 in. (2 cm) of sand. Before being put into contact with the pretreated water, the carbon was backwashed with carbon-filtered distilled water to remove fines and to stratify the bed. The pretreated water was pumped downward through the carbon columns at a flow rate of 1.1–1.5 gpm/sq ft (3–4 mL/min). Depending on the carbon depth, the empty bed contact time (EBCT) ranged between 1.0 and 2.0 min. The detailed experimental design and the rationale for the use of small-scale columns were discussed in a US Environmental Protection Agency report.[3]

The column effluent flowed into 100-mL glass collection chambers, the overflow from which flowed directly to a drain. The contents of the chambers were sampled manually twice a day.

Flow rates to the columns were checked every 12 h, and adjustments were made as necessary to ensure constant and equal flow rates to all columns. If the head loss buildup in a column reduced the flow rate to an unacceptable level, the column was taken out of service and backwashed with distilled water that had been carbon-filtered. To avoid extensive backwashing, the columns were returned to service as soon as the turbidity was flushed from them.

After collection, samples were adjusted

*Mini-Puls II, Model 42746-HP8, Gilson Medical Electronics Inc., Middleton, Wis.
†3400 series, Glenco Scientific Inc., Houston, Texas
‡50 × 80 Nuchar WV-G, Westvaco, Covington, Va.

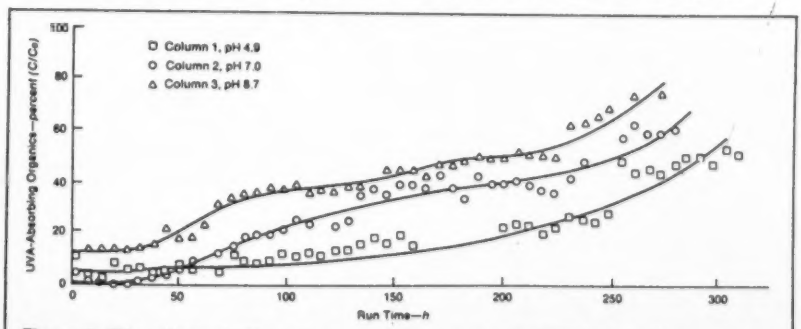


Figure 1. The effect of pH on the percentage removal of UVA-absorbing organics by GAC *(flow rate—5.0 mL/min; pH of coagulation—5; alum dose—100 mg/L; average UVA feed—0.28; path length—50 mm; wavelength—254 nm)*

NTIS is authorized to reproduce and sell this report. Permission for further reproduction must be obtained from the copyright owner.

TABLE 1
The influence of adsorption pH on the time of breakthrough of 1 mg TOC/L

Adsorption pH	Run Time Determined From Figure 2 h	Run Time Determined From Figure 1 h
8.7	47	46
7.0	106	96
5.0	225	225

TABLE 2
Data used in optimum pH calculation

Parameter	Value
A	2×10^{-3} g-equiv/L
N	$0.30/kg
H	$0.30/kg
M	$1000/m^3
V	$5.73 \times 10^{-6} m^3$
H_o^+	$10^{-8.3}$ mol/L
Q	5.04 L/d

to pH 4 with sulfuric acid and stored for analysis. All analyses for a particular study were conducted at the same time to avoid errors caused by day-to-day variations in the instruments and in calibration procedures. All ultraviolet absorbance (UVA) and total organic carbon (TOC) analyses were conducted with samples at pH 4.

Analytical procedures. *Total organic carbon.* Total organic carbon was measured with an organic carbon analyzer.* This instrument employs ultraviolet radiation to oxidize organic matter to carbon dioxide, which is then measured by the increase in conductivity of a pure water reservoir maintained within the analyzer. The instrument proved reliable and provided accurate, reproducible data in the range of 0.1 to 8 mg TOC/L when the manufacturer's recommended techniques were followed.

Ultraviolet absorbance. In this study ultraviolet absorbance was monitored using an ultraviolet-visible spectrophotometer,† which used a 5-cm quartz cell at 254 nm.

Trihalomethane precursors. The trihalomethane (THM) formation potential was used in this study to quantify precursor concentration. Water samples were chlorinated for 48 h with excess free chlorine, and the resulting THM concentrations were measured by solvent extraction and gas chromatography‡ using an electron capture detector. The technique was previously described by Semmens and Field.[1]

Results

A sample of Mississippi River water was coagulated with 100 mg alum/L at pH 5 and filtered as described previously. The pH of the filtrate was then adjusted to different levels for each carbon column using sodium hydroxide or sulfuric acid. Three carbon columns were operated at pH values of 4.9, 7.0, and 8.7. A fourth column containing sand was employed as a control. The sand column measured 0.5 in. (1.5 cm) in internal diameter and contained a 3.9-in. (10-cm) depth of sand. The EBCT in the control column was approximately 5 min.

The breakthrough in UVA for the three carbon columns is presented in Figure 1. The curves clearly suggest that operation at a low pH improved the performance of the GAC columns and resulted in lower organics concentrations in the effluent. In addition, the breakthrough curves at lower pH values tended to rise less rapidly. The very shallow breakthrough curves gave rise to a large increase in breakthrough capacity for a desired level of organics removal as the pH was decreased.

The effluent from the control column showed a 17-percent decline in TOC from the feed concentration of 3 mg/L. The effluent TOC from the carbon column operated at pH 8.7 reached the same level as the control column after 200 h of operation, suggesting that essentially complete breakthrough had been accomplished.

The UVA data in Figure 1 may be compared with the TOC removal data presented in Figure 2. The TOC curves show the same effect and compare favorably with the UVA removal data, although the magnitude of the removals was different and depended on the way the organics concentrations were measured. The initial TOC breakthrough was approximately 0.5 mg/L at pH 8.7. If the run time after which the effluent TOC rose by 0.5 mg/L to the 1-mg/L level is evaluated, some interesting comparisons can be made. Drawing a horizontal line across Figure 2 at the 1-mg TOC/L level provides the breakthrough times for the different operating pH values shown in Table 1.

Since it was noted that UVA was equal to 0.065 for an effluent TOC of 1 mg/L, Figure 1 can also be used to evaluate run times. This UVA value gave the breakthrough times also reported in Table 1.

These data clearly demonstrate that for an effluent value of 1 mg TOC/L, the operating capacity of a carbon column can be increased by a factor of 400 to 500 percent by reducing the pH of adsorption from 8.7 to 5.0. To verify the behavior observed in Figures 1 and 2, another test was conducted in which the adsorption pH was varied between 5.0 and 8.7. This test was also conducted with Mississippi River water that had been treated with 100 mg alum/L at pH 5. EBCT was 1.15 min, and, as may be seen in Figure 3, the results were similar to those presented in Figure 2.

Operating under lower pH conditions may impose troublesome constraints on construction materials in order to avoid corrosion, but the long-term reduction in operating costs may outweigh the higher initial capital costs. The analysis will be influenced strongly, however, by the desired treatment objective. For example, if an effluent concentration of 2 mg TOC/L could be tolerated for this system, the operating capacity would only be increased by approximately 100 percent if the pH was reduced from 8.7 to 5.0.

The influence of pH on the removal of THM precursors by the carbon columns was also evaluated in the duplicate test. Samples of effluent from the carbon columns were chlorinated, and measured THM formation potentials (THMFPs) were plotted as a function of run time for the different carbon columns (Figure 4). The results indicate that THM precursor removal showed the same trend as TOC removal. Examination of brominated THMs in the column effluents indicated that dibromochloromethane formation was not influenced significantly by pH and varied between 0.3 and 1.2 $\mu g/L$ throughout the run. Bromodichloromethane formation was reduced effectively by GAC treatment. Effluent concentrations of THMFP were observed to increase with run time and as the feed solution pH was increased from 5.0 to 8.7. Bromoform concentrations in the column effluents were negligible in all cases, and chloroform accounted for the majority of the trihalomethanes that were formed.

Discussion

The organic content of Mississippi River water at Minneapolis-St. Paul, Minn., is composed principally of neutral and acidic organic compounds,[4] 40 percent of which were classified as hydrophobic and 60 percent as hydrophilic according to the technique developed by Leenheer and Huffman.[5] The molecular weight distribution of the river water was evaluated by ultrafiltration, which indicated that the molecular weight fractions <1K, 1–10K, 10–100K, and >100 K contained 23, 50, 10, and 1 percent of the organic content, respectively. Approximately 60 percent of the TOC can be removed by coagulation with alum. During alum coagulation, high-molec-

*Photochem Organic Carbon Analyzer, Barnstead Co., Boston, Mass.
†Model 26, Beckman Instruments, Fullerton, Calif.
‡Model 5840A, Hewlett Packard, Palo Alto, Calif.

ular-weight organics are removed and the majority of the residual organic content is <1 K in molecular weight. In addition, the organic content of the coagulated water is characterized as being approximately 70 percent hydrophilic, and 30 percent hydrophobic acids and neutrals.[4]

The influence of pH on the adsorption behavior of GAC may have stemmed from the acidic character of a fraction of the organics being removed. The ionic form of carboxylic acids is more poorly adsorbed than the undissociated acid molecules.[6-8] This difference may stem from the increased solubility of the ionized species or may be explained in terms of the mechanism of adsorption. The surface of activated carbon is negatively charged in the neutral pH range as a result of the dissociation of surface carboxylic groups. A reduction in pH can be expected to improve adsorption since the protonation of carboxylic functional groups on both the organic acids in solution and the carbon surface reduces electrostatic repulsion forces, thus promoting a greater degree of adsorption.

If the influence of pH were restricted to its impact on carboxylic functional groups, then the pH effect would only be significant below pH 6 since the pK_a of carboxylic functional groups ranges between 2 and 5. However, the carbon surface apparently changes in character as the pH is altered in the neutral range. For example, Ward and Getzen[7] found that the adsorption of several aromatic acids, including phenoxyacetic acid, showed a very strong pH dependence in the pH range 5 to 9. In this range, the adsorption capacity of phenoxyacetic acid decreased by a factor of 4 to 5. However, the pK_a of the acid is 3.03, and the phenoxyacetate ions predominated over this entire pH range. The reduction in adsorption capacity with increasing pH could be explained if weakly acidic functional groups on the carbon surface dissociated in this pH range, because the increased negative surface charge would reduce adsorption capacity by virtue of increased electrostatic repulsive forces. At the higher pH values, it is possible that hydroxyl (OH) adsorption could also occur, further reducing adsorption capacity. However, Ward and Getzen[7] noted that the adsorption capacity for phenoxyacetate was not influenced by a pH >9.0, and it is unlikely, therefore, that significant competitive OH adsorption occurred in their study.

Snoeyink et al[9] studied the sorption of *p*-nitrophenol (PNP) and observed that the capacity of carbon for PNP decreased with increasing pH above that corresponding to a pK_a of 7.15. The decrease in capacity was greater than could reasonably be anticipated from solubility differences, and these authors argued that greater electrostatic repulsive forces at higher pH values may account for the observed effect. Increased negative surface charges at high pH values may have been caused by physical adsorption of OH or by dissociation of very weakly acidic surface functional groups.

Ward and Getzen[7] also noted that the adsorption of aromatic carboxylic acids was maximized when the solution pH was equal to the pK of the acid. These authors suggested that this can be explained if undissociated acid enhanced the adsorption of the acid anion. This synergistic effect was later discussed.[8]

Other investigators[8,10] have examined the behavior of organic compounds that do not dissociate at low pH. Snoeyink et al[9] observed that phenol adsorption

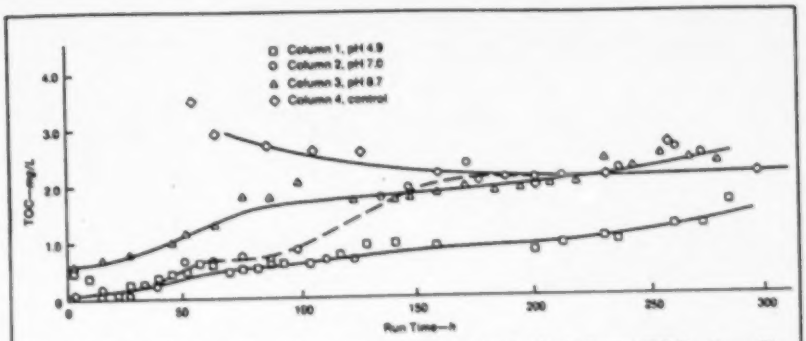


Figure 2. The effect of pH on the removal of TOC by GAC *(influent TOC—3 mg/L; flow rate—5 mL/min; pH of coagulation—5; alum dose—100 mg/L)*

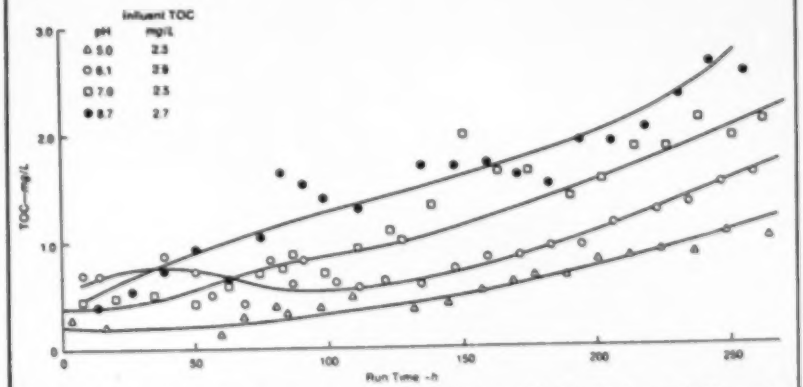


Figure 3. The effect of pH on the removal of TOC by GAC *(pH of coagulation—5; alum dose—100 mg/L; EBCT—1.15 min)*

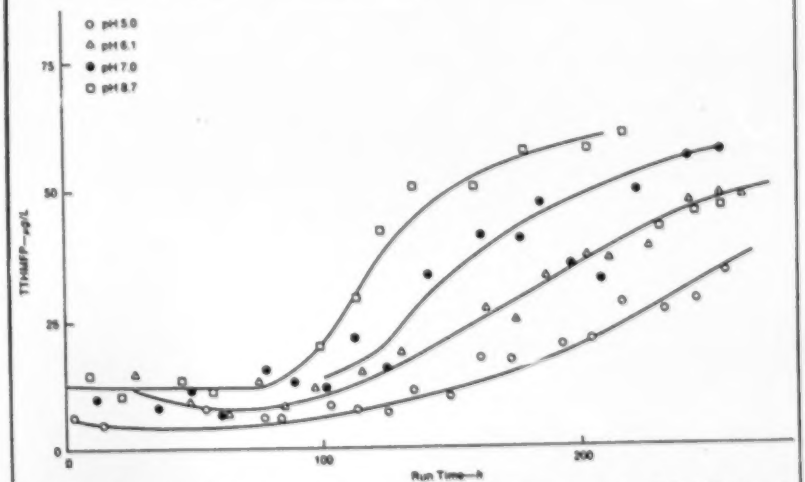


Figure 4. The effect of pH on the removal of THM precursors by GAC *(influent TTHM formation potential—101 μg/L; alum dose—50 mg/L; pH of coagulation—5; EBCT—1.15 min)*

decreased when the pH was reduced from 7.5 to 5.6. The authors argued that since no change in the character of phenol occurred in this pH range, the behavior was attributable in part to the competitive effect of the increased quantity of acid sorbed with decreasing pH. They cited evidence at carbonyl oxygen sites. At low pH, protons may interact competitively with carbonyl oxygen to desorb phenol.

The adsorption behavior of the complex mixture of naturally occurring organic compounds as a function of pH is a little more difficult to explain than the single solute results. However, the single solute studies provide insights and suggest possible mechanisms that may help explain the observed behavior of complex mixtures.

In the pH range 5 to 9, it is likely that both the carbon surface charge and the degree of dissociation of the organic content of water will vary. As the pH is increased, the carbon surface will become more negative, and weakly acidic groups, such as phenolic groups, on the organics may dissociate, rendering the organics more negative.[11] This will tend to bring about a reduction in adsorption capacity as the pH is increased.

Black and Christman[12] studied the character of humic substances in colored surface water and found that the particle size increased and the concentration of particles decreased as the pH decreased. These changes in the character of naturally occurring organics may be significant. The studies of Ward et al[7,8] and Snoeyink et al[9] suggest, however, that in this pH range, the change in the character of the carbon may be more significant than any change in the character of the organics.

The influence of pH on the removal of TOC from river water may vary for different carbons and even for the same carbon following regeneration. Coughlin and Tan[13] showed that the functional groups on the carbon surface may have a significant impact on adsorptive capacity. For example, carboxylic functional groups tended to reduce the adsorptive capacity of carbon for phenol. Different carbons, as well as the same carbon exposed to different solution conditions, will have different concentrations of surface functional groups. For example, exposure of a carbon to either hypochlorite or permanganate, both of which are used in water treatment plants, may increase the concentration of surface carboxyl groups. These changes in the surface chemistry of carbon can be expected to cause different responses to changing pH conditions for a given water.

The cation composition of the pretreated waters was not significantly affected by pH adjustments in the range considered in this study. Although divalent metal ions such as calcium (Ca^{2+}) and magnesium (Mg^{2+}) may influence the extent of organics adsorption, these ions were always present in concentrations $>10^{-3}$ *M*. Randtke and Jepsen[14] found that these ions had a significant impact on organics adsorption only when their concentrations fell below 10^{-3} *M*. It is unlikely, therefore, that any change in the Ca^{2+} or Mg^{2+} composition could have significantly influenced adsorption behavior in these studies.

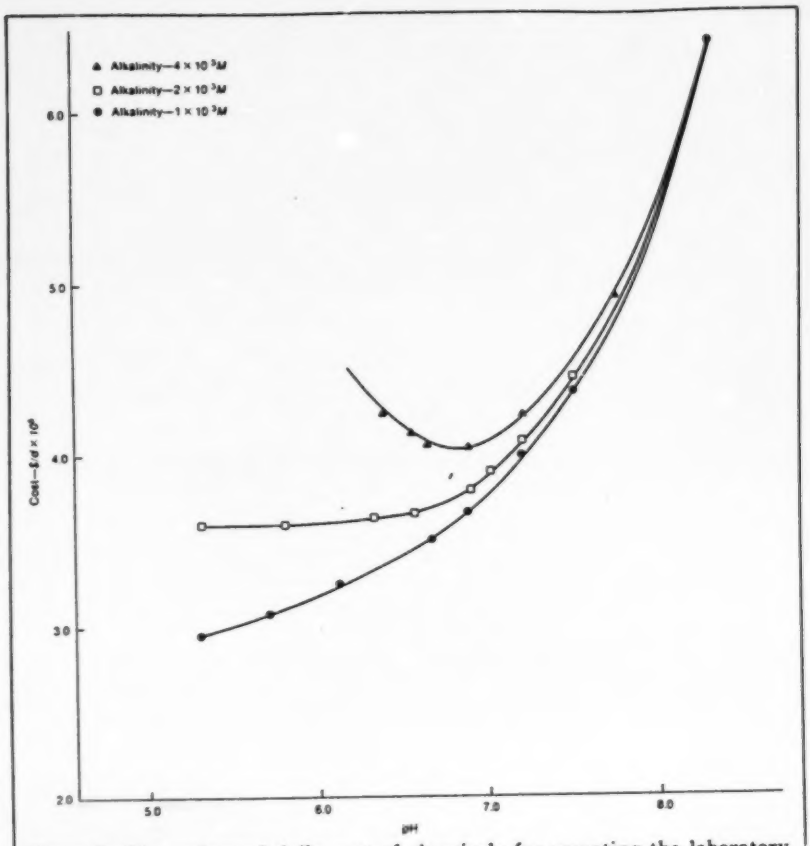


Figure 5. The estimated daily cost of chemicals for operating the laboratory carbon columns as a function of pH *(treatment objective—effluent TOC of* <1 mg/L)

Optimum pH. The influence of pH adjustment on carbon column performance is sufficiently great that it may be beneficial for a water treatment facility to consider pH reduction prior to GAC adsorption. To avoid corrosion problems in the distribution system, the GAC-treated water would have to be stabilized by adding alkali. The cost of pH control therefore includes the combined cost of adding acid to reduce the pH and adding alkali to restore a stable pH following GAC treatment. The cost of GAC treatment decreases as the bed life of the carbon is extended, and it will, therefore, decrease as the pH is reduced. It is likely, however, that an optimum pH would minimize the overall cost of treatment. Below this pH value, the cost of additional acid and base would exceed the benefit gained from extended carbon life.

A simple example calculation of the optimum operating pH for the mini-columns is based on the performance curves depicted in Figures 2 and 3. It is assumed that (1) the capital costs of the carbon columns and pretreatment operations are independent of operating pH, (2) only chemical costs are considered, (3) the treatment objective is <1 mg TOC/L in the GAC column effluent, (4) the system is closed (no carbon dioxide $[CO_2]$ escapes when acid is added to the water), (5) all the alkalinity is bicarbonate, and (6) sulfuric acid (H_2SO_4) and sodium hydroxide (NaOH) are employed for pH control.

For purposes of the analysis, H = cost of H_2SO_4 ($/kg), N = cost of NaOH ($/kg), $[A]$ = alkalinity (g-equiv/L), $[H_o^+]$ = initial hydrogen ion concentration (mol/L), $[H_F^+]$ = final hydrogen ion concentration (mol/L), and $[L]$ = acid added (g-equiv/L).

The cost of pH control is

$$C_{pH} = C_{acid} + C_{base}$$

in which C_{acid} = the cost of the acid required to reduce the pH to the desired level per unit of time, and C_{base} = the cost of the base required to raise the pH to the desired level for distribution per unit of time.

$$C_{pH} = 0.049\,QLH + 0.040\,QLN \quad (1)$$

in which 49 and 40 are the equivalent weights of the acid and base, respectively; the base added is that required to neutralize the added acid; and Q is the flow rate of water treated (L/d).

Assuming $[L] < [A]$, the pH value for the treated water can be calculated from the carbonate equilibrium:

$$[H_F^+] = ([L]10^{-6.3})/([A] - [L]) + ([H_o^+][A])/([A] - [L]) \quad (2)$$

A relationship can be derived from Figure 3 to relate service time T (h) to the operating pH (pH_F) for a specific treatment objective. When it is assumed, for example, that the treatment objective is <1 mg TOC/L in the effluent at all times, then for the pH range 5.0–8.7, the data in Figure 3 fit the equation:

$$T = 47(10.05 - pH_F) \quad (3)$$

Substituting pH_F in Eq 3 yields an expression in which T is a function of the amount of acid added to the water:

$$T = \left[(10.05 + \log \left\{[L]10^{-6.3}/[A] - [L]) + ([H_o^+][A]/[A] - [L])\right\}\right] \quad (4)$$

The cost of the activated carbon per day C_c can be estimated by dividing the cost of the carbon by its service life T:

$$C_c = 24\,(VM/T)$$

in which V = carbon bed volume (m^3), and M = carbon cost ($/m^3).

By combining the costs of acid and base with the cost of carbon, the overall chemical cost can be calculated. By combining equations, the overall cost function C_T can be expressed:

$$C_T = 0.049\,QLH + 0.04\,QLN + \left\{(24VM)/\left(47\left[10.05 + \log\left\{([L]10^{-6.3})/([A] - [L]) + ([A][H_o^+])/([A] - [L])\right\}\right]\right)\right\} \quad (5)$$

Q and V are not variable, because the relationship for T (Eq 3) is specific for the flow rate and column size studied. If more data were available to interrelate the EBCT, pH, and service life of the GAC column, then T could be expressed as a function of the variables V, Q, and pH for a given treatment objective. Additional studies are needed.

By substituting the data shown in Table 2 into the cost function, the overall cost of treatment can be calculated as a function of the amount of acid added (L) or the operating pH (pH_F). The optimum pH is dependent on the relative costs of acid, base, and carbon and also on the alkalinity of the water. As the alkalinity is increased, the optimum pH will increase because the cost of reducing the pH increases. In addition, however, the shape of the cost function is altered as shown in Figure 5. When the alkalinity was low ($10^{-3}M$, 50 mg as $CaCO_3$/L), an optimum pH was not identified; the cost of treatment continued to decrease as the pH decreased. In such cases the operating pH should be as low as possible within the constraints imposed by construction materials. When the alkalinity was somewhat higher ($2 \times 10^{-3}M$), the cost function indicated that a significant benefit was to be gained by reducing the pH from 8.3 to 7.0, but no significant cost reduction was gained by operating at lower pH values. An alkalinity of $4 \times 10^{-3}M$ (200 mg as $CaCO_3$/L) caused the cost function to exhibit a well-defined optimum pH at about pH 6.8.

This analysis was meant to illustrate the concept of optimum pH and the importance of pH as an operating parameter in treatment plants that use activated carbon. In practice, however, the optimum operating pH is strongly dependent on both the level of pretreatment and the actual treatment objective. More lenient standards for finished-water quality would reduce the rate of carbon consumption and lower daily carbon costs. In addition, the influence of pH on the percentage increase in service time may be less marked as standards for the effluent are relaxed. Both factors tend to increase the optimum operating pH. Nevertheless, this type of analysis is valuable for identifying the importance of pH as an operating parameter in plants where carbon adsorption is to be implemented.

Although these results cannot be extended to the treatment of other waters, the same approach may be applied. For example, in cases in which coagulation–flocculation precedes activated carbon adsorption, the coagulant dose will affect the solution pH and the organic content of the influent to the carbon columns. Since coagulants such as alum are acidic, they will reduce the cost of adding acid. The carbon service life T will be extended because the organic content of the influent will be reduced by higher coagulant doses.[15]

The assumption of a closed system is probably fair because the conditions in a flocculation tank (the small air–water interface and the gentle mixing) are not conducive to the loss of CO_2. The pH of the water can be raised following carbon adsorption by stripping the CO_2 from solution. This would reduce the amount of base required for pH stabilization and might also reduce the concentration of low-molecular-weight volatile organics in the product water.

Conclusions

The reduction of organics by coagulation improves dramatically as the pH is decreased to 5. The combined effects of pH on coagulation and on adsorption highlight the need for effective pH control.

Acknowledgment

The authors acknowledge the financial support of the US Environmental Protection Agency, grant CR806377.

References

1. Semmens, M.J. & Field, T.K. Coagulation Experiences in Organics Removal. *Jour. AWWA*, 72:8:476 (Aug. 1980).
2. Organics Removal by Coagulation. *Jour. AWWA*, 70:10:588 (Oct. 1979).
3. Semmens, M.J. et al. Optimizing Coagulation-Adsorption for Haloform and TOC Reduction. USEPA CR806377 (1982).
4. Semmens, M.J. & Staples, A.B. The Nature of Organics Removed During Treatment of Mississippi River Water. *Jour. AWWA*, 78:2:76 (Feb. 1986).
5. Leenheer, J.A. & Huffman, E.W.D. Jr. Classification of Organic Solutes in Water by Using Macroreticular Resins. *Jour. Res. USGS*, 4:6:737 (1976).
6. Weber, W.J. *Physicochemical Processes for Water Quality Control*. Wiley Interscience, New York (1972).
7. Ward, T.M. & Getzen, F.W. Influence of pH on the Adsorption of Aromatic Acids on Activated Carbon. *Envir. Sci. & Technol.*, 4:1:64 (1970).
8. Ward, T.M. & Getzen, F.W. A Model for the Adsorption of Weak Electrolytes on Solids as a Function of pH. Part 1. Carboxylic Acid-Charcoal Systems. *Jour. Colloid and Interface Sci.*, 31:4:441 (1962).
9. Snoeyink, V.L.; Weber, W.J.; & Mark, H.B. Jr. Sorption of Phenol and Nitrophenol by Active Carbon. *Envir. Sci. & Technol.*, 3:10:918 (1969).
10. Myers, A.L. & Zolandz, R.R. Effect of pH Upon Multicomponent Adsorption from Dilute Aqueous Solution. *Activated Carbon Adsorption of Organics From the Aqueous Phase*, Vol. I (I.H. Suffet and M.J. McGuire, editors). Ann Arbor Sci. Publ., Ann Arbor, Mich. (1980).
11. Schnitzer, M. & Kodana, H. Montmorillinite: Effect of pH on Its Adsorption of a Soil Humic Compound. *Science*, 153:70 (1966).
12. Black, A.P. & Christman, R.F. Characteristics of Colored Surface Waters. *Jour. AWWA*, 55:6:753 (June 1963).
13. Coughlin, R.W. & Tan, R.N. Role of Functional Groups in Adsorption of Organic Pollutants on Carbon. Water 1968, Chem. Engrg. Progr. Sym.
14. Randtke, S.J. & Jepsen, C.P. Chemical Pretreatment for Activated Carbon Adsorption. *Jour. AWWA*, 73:8:411 (1981).
15. Semmens, M.J. et al. Organic Removal from Mississippi River Water—Influence of Coagulation Pretreatment on Adsorption (unpublished).

About the author: *Michael J. Semmens is associate professor of environmental engineering, Department of Civil and Mineral Engineering, University of Minnesota, 500 Pillsbury Drive S.E., Minneapolis, MN 55455-0220.*

NOTICE

This document has been reviewed in accordance with U.S. Environmental Protection Agency policy and approved for publication. Mention of trade names or commercial products does not constitute endorsement or recommendation for use.

This article documents research that was conducted under the auspices of the U.S. Environmental Protection Agency (USEPA). As an arm of the government, the USEPA has a paid up, non-exclusive, irrevocable, worldwide license to reproduce, prepare derivative works, and distribute to the public all of the material contained herein, and to grant others acting on its behalf the right to do so. The USEPA grants to the National Technical Information Service, Department of Commerce, the right to act as its agent in the distribution of this material.